Characterization and sampling strategy of radioactive aerosols in zircon industries

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Abstract
A material containing a significant amount of natural radioactive nuclides is referred to as a naturally occurring radioactive material (NORM). Workers who handle industrial materials containing NORMs at significant concentrations are at risk of being exposed to radiation at considerable levels. When assessing the effective dose to workers following radioactive aerosols inhalation exposures, significant reductions in dose uncertainty can be achieved through direct measurement of the aerosol characteristics. In the present study, the particle size distribution of the ambient aerosol was measured, at various locations in a refractory materials processing plant, using a static and a personal air sampling. Results were then used to illustrate the influence of the airborne particle size distribution on the internal dose estimation.

1. INTRODUCTION

Zirconium is the 18th most abundant element in the Earth crust. It occurs in nature as the free oxide ZrO_2 (baddeleyite), but most commonly as zircon, a compound oxide with silica having the chemical formula $ZrSiO_4$. Most of the commercially useful deposits of zircon are in beach sands, found in Australia, South Africa, India, Ukraine and the United States of America. Zircon has a very high melting point and a high chemical resistance. With these properties the mineral finds uses in refractories, foundry sands and in the ceramic field. Zircon contains low levels of uranium and thorium up to 0.1%, introduced into the crystal lattice during the crystallization process of the zircon from the molten rock. These elements replace the Zr atoms in the lattice and are, therefore, bound very strongly into the mineral structure. It is not possible to remove the uranium and thorium without total destruction of the crystal lattice. These elements imply the presence of radioactive isotopes from the naturally occurring ^{238}U and ^{232}Th decay series. Over the past 20 years, many countries have started programs or taken measures to regulate exposures from NORM found in a variety of sources. The International Basic Safety Standards for Protection against Ionizing Radiation and for the Safety of Sources [1] and the European Council Directive of May 1996 (96/29/EURATOM) [2] contain provisions for protective measures against significant exposures resulting from radioactive natural sources.
Handling zircon can generate airborne dust, leading to the possibility of inhalation of zircon particles by workers involved in such operations. Experience in the internal exposure monitoring used in this type of industry is growing and practical guidance for zircon users has begun to appear: the safety reports issued by IAEA [3] and the SMOPIE reports [4] are especially acknowledged. This study forms part of the improvement of workers surveillance. The aim of this project is to develop a monitoring strategy, using a personal sampling, to assess risks of internal exposures in zircon industries.

A number of researchers [5-7] have made estimates of potential radiation dose that could result from working with zircon. The predicted dose levels strongly depend on assumptions. We verified, in this study, some hypothesis in particular the contribution of radon in the effective dose and the relevance of using, in refractory industry, the default diameter recommended by the International Commission on Radiological Protection (ICRP). For this, a Respicon instrument was used, as a personal sampler, to characterize the particle size distribution of the ambient aerosol. Results were then used to illustrate the influence of the size distribution on the internal dose estimation.

2. DESCRIPTION OF THE FACTORY

The factory is located in the south of France. It produces, as its main business, electrofused refractory blocks used for the construction of smelting ovens for glass. The zircon sand is used as a raw material and is stored in large reinforced-concrete tanks. Zircon sand (or a semi-finished product based on zircon, for example zircon–mullite or 'scraps' from the finishing process) is mixed with alumina and sodium carbonate before being smelted in the oven. The molten material is poured into moulds and, the finished blocks are stored for cooling during fifteen to twenty days in the cooling area. They are then moved to another room where they are sand-blasted, ground, polished with emery, finish ground and finally cut. The accurate assembly of all the components of each oven is then checked in the pre-assembly area. The plant also manufactures ceramic beads for impact surface treatment applications by a unique fusion process at very high temperature. The molten material is finely divided and then left for cooling. Beads are classified by sieving or by dynamic selection. Bagging of beads is carried out into big bags without special dust extraction.
The resulting scraps are milled in readiness for reintroduction into the manufacturing process. As there is potential for dust generation at various steps in the process, dust extraction systems were installed where the mixture is produced and smelted.

3. EXPOSURE PATHWAYS

The exposure pathways to workers that are most likely to require consideration in the zircon industries are those involving external exposure to gamma radiation emitted from bulk quantities of zirconium-containing material and internal exposure via the inhalation of radionuclides in zirconium-containing dust or in furnace fumes. Internal exposure via the inhalation of radon may also need to be considered. Measurable gamma exposure may occur whenever bulk zircon feedstock or product is present. Dose will be dependent on distance from the radiation source and time of exposure and may be reduced by limiting access to bulk storage areas. This study focuses exclusively on internal exposure of workers by aerosol inhalation.

4. RADON AND THORON PROGENY EXPOSURE

Radon (^{222}Rn) gas concentration in air was measured in three locations using an AlphaGUARD®, Model Genitron 2000. The sampling points, identified as having potential for workers inhalation exposures to radiation, are oven operation cabin, beads sorting and zircon storage areas. The instrument was operated

continuously for several months, from 30th Mars to 20th December. The values were recorded every 60 minutes. Results show that radon gas concentration at these different locations of the plant varied between 1 $Bq.m^{-3}$ and 64 $Bq.m^{-3}$ with a mean value of 25 $Bq.m^{-3}$. Natural background radon concentration was measured earlier in an office, away from the plant, and the mean value was 20 $Bq.m^{-3}$. A Tracerlab® was used, at the same places and during the same period of time, to measure Potential Alpha Energy Concentration (PAEC) due to the short lived radon and thoron decay products. Measuring cycle was set to 60 minutes. Results show insignificant PAEC with a mean value of 29.6 $nJ.m^{-3}$ for radon and 7.39 $nJ.m^{-3}$ for thoron. Those low radon concentration and PAEC values observed in this study can be explained by a low emanation of the gas from the minerals and high ventilation in the plant.
Righi et al. [7] found that the effective dose from radon and its decay products in a zircon processing plant was 0.6 $mSv.y^{-1}$ and therefore, they take it into account. But, low exposure to radon was obtained in other studies carried out in facilities involving the use of zircon sand [5, 6]. In our study, since radon natural background is at the same level as radon concentration in the plant, dose contribution by this exposure pathway will be considered negligible.

5. CHARACTERIZATION OF AMBIENT AEROSOL

There is a likelihood of variation in particle size during each stage of operation due to different nature of processes involved. The ICRP has considered default particle size as 5 µm Activity Median Aerodynamic Diameter (AMAD) and a geometric standard deviation (GSD) of 2.5 for working out dose coefficients for different radionuclides. This recommended value is considered to be more representative of workplace aerosols, especially in nuclear industry. But, it may not be representative of the particle size distribution of the aerosols produced in certain industries. Consequently, using recommended default values for particle size distribution can introduce a bias in the dose estimation. Kim et al. [8] state that, for this reason, site-specific particle size distribution should be determined whenever possible to reduce this source of bias in the dose assessment. A study, combining static and personal air sampling, was thus carried out to characterize the ambient aerosol. Aerosol sampling was conducted in the same locations selected for radon and thoron measurements. Studies included measurement of particle size distribution by Andersen cascade impactor and Respicon sampler. The cascade impactor consists of 8 impactor stages and a final collection filter thus partitioning particles into 8 different size ranges. The aerodynamic cut-off sizes of each stage were 9.0 µm, 5.8 µm, 4.7 µm, 3.3 µm, 2.1 µm, 1.1 µm, 0.65 µm and 0.43 µm from the zero to the seventh stage, respectively [9]. A backup filter is provided at the end of impactor to collect all the particles escaping out of the impactor stages. We assumed that the upper and lower particle size limits are 20 µm and 0.03 µm.
The Respicon manufactured by Helmut Hund GmbH is a 3.1 $L.min^{-1}$ three-stages virtual impactor with an annular slit aerosol inlet (figure 1a). The instrument has been developed to simultaneously collect the three conventional fractions: inhalable, thoracic and respirable. It can be used as either a personal or an area sampler. It can provide samples not only for gravimetric analysis but also radiological and chemical analyses. A detailed description of the instrument has been published previously [10]. Inside the Respicon, as shown in figure 1b, particles collected on filter on the first stage represent the respirable fraction, the second stage represent the tracheobronchial fraction, the third stage represent the extrathoracic fraction and all three filters represent the inhalable

fraction. The cut-off diameters of the first and the second stage are 4 µm and 10 µm respectively.
When used as a free-field area sampler, the performance of the Respicon matches the three conventional fractions quite accurately, as shown by Li et al. [11] who assessed the instrument in a small wind tunnel at wind speeds of 0.55 $m.s^{-1}$ and 1 $m.s^{-1}$ using test aerosols of different sizes in the range of 1 µm to 68 µm.

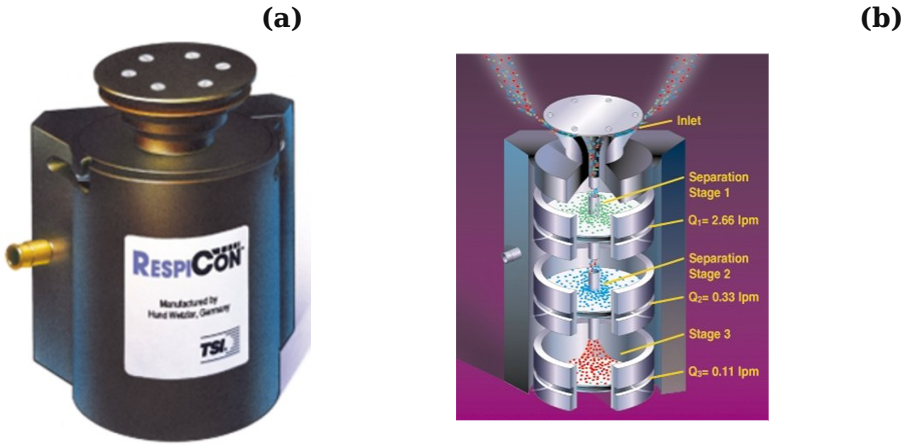

Figure 1: (a) Picture and (b) inside schematic drawing of a Respicon sampler

5.1 Static air sampling

Aerosol sampling was conducted using the Andersen cascade impactor at a flow rate of 28.3 $L.min^{-1}$ and the Respicon sampler at a flow rate of 3.1 $L.min^{-1}$ installed near each other. Glass fibre filter was used as collection substrate for the Andersen cascade impactor. The Respicon was loaded with three membrane Teflon filters contained in the special filter holders supplied with the instrument. These filters have the advantage (for alpha counting) that they retain particles on their surface. Prior to loading in the devices, filters were weighed using a Sartorius microbalance with a sensitivity of ±3 μg. Prior to sampling, the flow rates were checked for both instruments with a TSI flowmeter and verified to be within manufacturers' specifications. The sampling duration was selected to get sufficient particles and to avoid the re-entrainment of particles from the cascade impactor filter. Sampling periods were taken between 8 h and 24 h depending on the location. After sampling, the filters were removed from the samplers and brought back to the laboratory where they are weighed again.

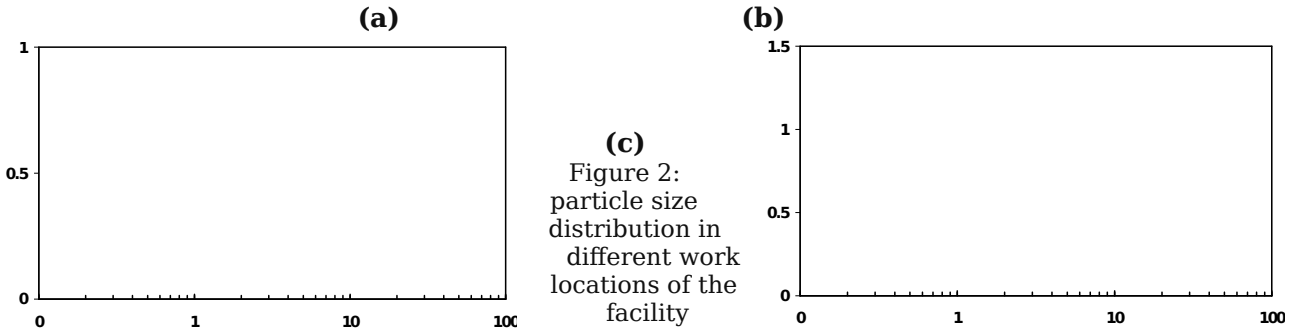

Figure 2: particle size distribution in different work locations of the facility

(a): oven operation cabin, (b): beads sorting area and (c): storage area

Figure 2 displays the aerosol size distribution measured with the Andersen cascade impactor. Results show that particle size varied over a wide range, from sub-micron sizes to more than 9 µm. In the oven operation cabin and beads sorting area, the particle size distribution was bimodal with a fine mode corresponding to particles collected on the last two stages and the final collection filter and a coarse mode corresponding to particles larger than 1µm. Similar results were obtained in a factory in Italy producing Alumina-Zirconium-Silica (AZS) blocs and using zircon sand as raw material [12]. Storage area shows only a coarse mode. The mass fractions obtained with the Andersen cascade impactor and the Respicon are presented in Table 1 and Table 2 respectively. Results show that data obtained with both instruments are in good agreement.

Table 1: mass fraction of dust in the atmosphere of the three selected workplaces

Sampling point	Mass fraction (%)	
	Fine mode	Coarse mode
Oven operation cabin	84	16
Beads sorting area	41	59
Storage area	2	98

Table 2: mass fraction in the three Respicon stages (static air sampling)

Sampling point	Mass fraction (%)		
	First stage	Second stage	Third stage
Oven operation cabin	74	0	26
Beads sorting area	37	20	43
Storage area	11	26	63

5.2 Personal air sampling

The use of static sampling does not ensure a representative measurement of the worker’s exposure. Thus, in order to assess what a worker breathes in during his job, surveys of exposure are conducted using the Respicon as a personal sampler. The aspiration orifice was placed in the breathing zone of the worker. The Respicon sampler requires a high capacity personal pump to maintain a 3.1 $L.min^{-1}$ flow rate. SKC pump was used. It was attached to the employee's belt, positioned so that it does not interfere with the work operation. The flow rate was verified both at the beginning and at the end of the sampling. For any individual worker, dust sampling was usually undertaken for 6 to 8 hours. As the plant operates with rotating shift schedule, the Respicon is carried, for each workplace, by three operators who take turns. After the sample was collected, mass concentration was calculated and alpha counting of filters was made. The mass fractions obtained with the Respicon are presented in Table 3.

Table 3: mass fraction in the three Respicon stages (personal air sampling)

Sampling point	Mass fraction (%)		
	First stage	Second stage	Third stage
Oven operation cabin	14	24	62
Beads sorting area	12	30	58
Storage area	14	39	47

We observe that mass fractions obtained by personal air sampling are very different from those taken by static air sampling.

5.2.1 Concentration

Mass of collected dust, along with the Respicon stage flow rates, and sampling times were used to calculate the mass concentrations of particles collected on the first stage (C_1), the second stage (C_2) and the third stage (C_3). These calculations were done according to the equations proposed by the Respicon manufacturer [13], and the calculations were done with the application of the correction factor of 1.5 recommended by the manufacturer for the third stage. The results are summarized in Table 4.

Table 4: mass concentrations of different dust fractions in three selected workplaces

Sampling point	C_1 (mg m^{-3})	C_2 (mg m^{-3})	C_3 (mg m^{-3})
Oven operation cabin	0.10	0.14	0.56
Beads sorting area	0.14	0.29	0.86
Storage area	0.35	0.86	1.52

5.2.2 Alpha counting

Radioactivity in the dust, sampled on each Respicon filter, was determined by alpha spectrometry system using a semiconductor detector. Counts were made over a period of 18 h. The counts were corrected for background and for the measured efficiency of the counting system, and then expressed in $Bq.g^{-1}$ of alpha activity. Results are listed in Table 5 and provide clear evidence of the enrichment of ^{210}Po in the furnace dust. This can be explained by the fact that the high temperature fusion process is conducted at about 2,200 ºC and it is expected that volatilization of radionuclides, particularly the ^{210}Po and the ^{210}Pb, will occur. In addition, we observe that the mass activity is higher for small particles. Results show also that during the process, there is a strong possibility that the decay chain equilibrium present in the zircon feedstock will be significantly disrupted.

Table 5: alpha specific activity of different dust fractions in three selected workplaces

Sampling point		Alpha activity (Bq g^{-1})		
		^{238}U	^{226}Ra	^{210}Po
Oven operation cabin	First stage	64.49	37.64	117.69
	Second stage	36.50	29.80	59.40
	Third stage	19.50	11.56	26.06
Beads sorting area	First stage	39.41	25.06	22.13
	Second stage	15.49	9.99	15.36
	Third stage	9.11	5.63	7.13
Storage area	First stage	15.62	11.90	7.85
	Second stage	6.12	4.97	3.48
	Third stage	5.25	2.99	2.12

6. EXAMPLE OF DOSE CALCULATION

The following formula gives the internal effective dose depending on the characteristics of aerosol sampled at each Respicon stage. For each stage, this dose can be estimated by:

$$Dose(mSv) = \sum_i e_i(AMAD,GSD) \times A_i(AMAD,GSD) \times C \times B \times t_E$$

where $e_i(AMAD,GSD)$ is the dose coefficient of the ith radionuclide (mSv.Bq^{-1}), $A_i(AMAD,GSD)$ is the airborne alpha mass activity of the ith radionuclide (Bq.g^{-1}), C is the mass concentration (mg.m^{-3}), B and t_E are the ventilation rate of the worker (m^3.h^{-1}) and the duration of exposure (h) respectively.

Table 6: Particle size distribution used for dose calculation, AMAD expressed in µm

Stage	Oven operation cabin		Beads sorting area		Storage area	
	AMAD	GSD	AMAD	GSD	AMAD	GSD
First stage	0.3	2.5	0.3	2.5	4	2.5
Second stage	6	1.5	6	1.5	10	1.5
Third stage	16	1.5	16	1.5	20	1.5

Although only one sample was taken, a dose calculation was made to illustrate the need to know the actual AMAD. Calculations are based on experimental data and hypotheses on particle size distribution (Table 6). The dose conversion factors used are appropriate for a material type S except for the ^{210}Po and the ^{210}Pb in oven operation cabin and beads sorting area. We assumed that these radionuclides can be dissociated from the silicate matrix and therefore be classified type M and F, respectively. Dose coefficient for ^{226}Ra was considered with a low radon emanation. The values of dose coefficient are taken from SMOPIE reports [4]. It is assumed also that a worker would be occupied at the plant for 1,600 working hours in a year. Internal exposure in oven operation cabin, beads sorting and zircon storage areas are 1.04 mSv.y^{-1}, 0.76 mSv.y^{-1} and 0.70 mSv.y^{-1} respectively. If the default AMAD of 5 µm is applied, the dose will be 1.56 mSv.y^{-1}, 1.14 mSv.y^{-1} and 1.33 mSv.y^{-1} respectively.

7. CONCLUSION

Personal air sampling was carried out with a Respicon sampler to characterize the particle size distribution and to illustrate the influence of the size on the effective dose estimation. The AMAD was found to be different from the recommended 5 µm value for occupational exposure. An example of dose calculation, based on the results of a single sample, showed that the knowledge of the aerosol size distribution is needed in order to estimate an internal dose. Other measurements and calculations are ongoing to determine, as precisely as possible, the characteristics of the ambient aerosol and subsequently to improve the dose estimation. The measurements of radon at key locations indicate that the radon levels are not much different from the ambient background levels, and exposure through this pathway can be assumed to be negligible in the plant under study.

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